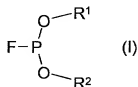


CLAIMS

We claim:

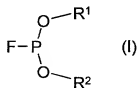
1. A catalyst system comprising comprising (1) a diorgano fluorophosphite ligand; and (2) rhodium, wherein the ratio of gram moles fluorophosphite ligand to gram atoms of rhodium is at least 1:1; and (3) a Group VIII metal, other than rhodium, or Group VIII metal-containing compound, in an amount effective to reduce the formation of HF during the use of the catalyst system.

2. A catalyst system according to Claim 1 wherein the diorgano fluorophosphite ligand having the formula

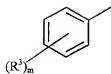


wherein R¹ and R² are separate or combined hydrocarbyl radicals having a total carbon atom content about 12 to 35; and the Group VIII metal is platinum, cobalt, ruthenium or palladium.

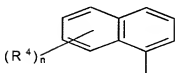
3. A catalyst system comprising (1) one or more fluorophosphite compounds having the general formula



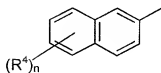
wherein R¹ and R² individually are independently selected from aryl groups having the formula:



(II)



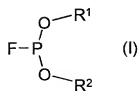
(III)



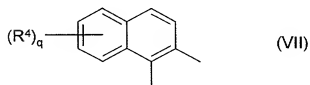
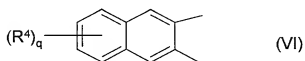
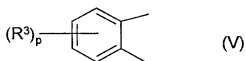
(IV)

wherein R^3 and R^4 are independently selected from alkyl, alkoxy, halogen, cycloalkoxy, formyl, alkanoyl, cycloalkyl, aryl, aryloxy, aroyl, carboxyl, carboxylate salts, alkoxycarbonyl, alkanoyloxy, cyano, sulfonic acid and sulfonate salts in which the alkyl moiety of such alkyl, alkoxy, alkanoyl, alkoxycarbonyl and alkanoyloxy groups contains up to about 8 carbon atoms; m and n each is 0, 1 or 2; the total carbon atom content of the hydrocarbonyl radicals represented by R^1 and R^2 is about 12 to 35; (2) rhodium wherein the ratio of gram moles fluorophosphite ligand to gram atoms rhodium is about 1:1 to 500:1; and (3) a Group VIII metal selected from platinum, cobalt, ruthenium or palladium wherein the gram atom ratio of the Group VIII metal:rhodium metal is in the range of about 1:1 to 5:1.

4. A catalyst system comprising (1) one or more fluorophosphite compounds having the general formula



wherein R^1 and R^2 collectively represent an arylene group having the formula



or a radical having the formula



wherein

each of A^1 and A^2 is an arylene radical having formula (V), (VI) or (VII) above wherein each ester oxygen atom of fluorophosphite (I) is bonded to a ring carbon atom of A^1 and A^2 ,

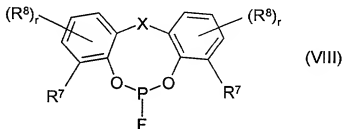
X is (i) a chemical bond directly between ring carbon atoms of A¹ and A²; or (ii) an oxygen atom, a group having the formula -(CH₂)_γ- wherein γ is 2 to 4 or a group having the formula



wherein R⁵ is hydrogen, alkyl or aryl; R⁶ is hydrogen or alkyl; and the group -C(R⁵)(R⁶)- contains up to about 8 carbon atoms; and

wherein R³ and R⁴ are independently selected from alkyl, alkoxy, halogen, cycloalkoxy, formyl, alkanoyl, cycloalkyl, aryl, aryloxy, aroyl, carboxyl, carboxylate salts, alkoxycarbonyl, alkanoyloxy, cyano, sulfonic acid and sulfonate salts in which the alkyl moiety of such alkyl, alkoxy, alkanoyl, alkoxycarbonyl and alkanoyloxy groups contains up to about 8 carbon atoms; p and q each is 0, 1 or 2; the total carbon atom content of the radical collectively represented by R¹ and R² is about 12 to 35; (2) rhodium wherein the ratio of gram moles fluorophosphite ligand to gram atoms rhodium is about 1:1 to 500:1; and (3) a Group VIII metal selected from platinum, cobalt, ruthenium or palladium wherein the gram atom ratio of the Group VIII metal:rhodium metal is in the range of about 1:1 to 5:1.

5. A catalyst system according to Claim 4 wherein the fluorophosphite ligand has formula (VIII)

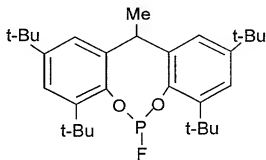


wherein R^7 represents hydrogen, halogen or C_1 to C_{12} alkyl; R^8 represents halogen, C_1 to C_{12} alkyl or C_1 to C_{12} alkoxy; r is 0, 1 or 2; and X is a group having the formula



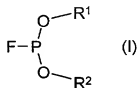
wherein R^5 is hydrogen, alkyl or aryl; and R^6 is hydrogen or alkyl and the ratio of gram moles fluorophosphite ligand to gram atoms rhodium is about 5:1 to 150:1.

6. A catalyst system according to Claim 5 wherein the dihydrocarbyl fluorophosphite compound has the formula:



wherein t-Bu is tertiary butyl and Me is methyl.

7. A catalyst solution comprising
(1) one or more dihydrocarbyl fluorophosphite compounds having the general formula

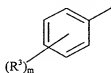


wherein R^1 and R^2 are aromatic hydrocarbyl radicals which contain a total of up to about 40 carbon atoms;

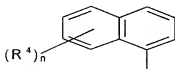
- (2) rhodium;
- (3) a Group VIII metal, other than rhodium, or Group VIII metal-containing compound, in an amount effective to reduce the formation of HF during the use of the catalyst system and
- (4) a hydroformylation solvent;

wherein the ratio of gram moles fluorophosphite ligand to gram atoms rhodium is at least 1:1.

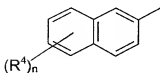
8. A catalyst solution according to Claim 7 wherein R^1 and R^2 individually are independently selected aryl groups having the formula:



(II)



(III)



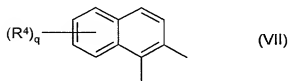
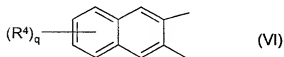
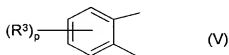
(IV)

wherein R^3 and R^4 are independently selected from alkyl, alkoxy, halogen, cycloalkoxy, formyl, alkanoyl, cycloalkyl, aryl, aryloxy, aroyl, carboxyl, carboxylate salts, alkoxycarbonyl, alkanoyloxy, cyano, sulfonic acid and

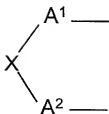
sulfonate salts in which the alkyl moiety of such alkyl, alkoxy, alkanoyl, alkoxy carbonyl and alkanoyloxy groups contains up to about 8 carbon atoms; m and n each is 0, 1 or 2; and the total carbon atom content of the hydrocarbyl radicals represented by R^1 and R^2 is about 12 to 35; the ratio of gram moles dihydrocarbyl fluorophosphite ligand to gram atoms rhodium is about 1:1 to 500:1; and the Group VIII metal is platinum, cobalt, ruthenium or palladium.

9. A catalyst solution according to Claim 8 wherein the ratio of gram moles dihydrocarbyl fluorophosphite ligand to gram atoms rhodium is about 5:1 to 150:1; the gram atom ratio of the Group VIII metal:rhodium is in the range of about 1:1 to 5:1; and the hydroformylation solvent is selected from alkanes, cycloalkanes, alkenes, cycloalkenes, carbocyclic aromatic compounds, esters, ketones, acetals and ethers and water which are liquid at the pressure at which the process is being operated.

10. A catalyst solution according to Claim 7 wherein R^1 and R^2 collectively represent an arylene group having the formula



or a radical having the formula



wherein

each of A¹ and A² is an arylene radical having formula (V), (VI) or (VII) above wherein each ester oxygen atom of fluorophosphite (I) is bonded to a ring carbon atom of A¹ and A²;

X is (i) a chemical bond directly between ring carbon atoms of A¹ and A²; or (ii) an oxygen atom, a group having the formula -(CH₂)_y- wherein y is 2 to 4, or a group having the formula



wherein R⁵ is hydrogen, alkyl or aryl; R⁶ is hydrogen or alkyl; and the group -C(R⁵)(R⁶)- contains up to about 8 carbon atoms;

R³ and R⁴ are independently selected from alkyl, alkoxy, halogen, cycloalkoxy, formyl, alkanoyl, cycloalkyl, aryl, aryloxy, aroyl, carboxyl, carboxylate salts, alkoxy carbonyl, alkanoyloxy, cyano, sulfonic acid and sulfonate salts in which the alkyl moiety of such alkyl, alkoxy, alkanoyl, alkoxy carbonyl and alkanoyloxy groups contains up to about 8 carbon atoms; p and q each is 0, 1 or 2;

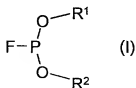
the ratio of gram moles dihydrocarbyl fluorophosphite ligand to gram atoms rhodium is about 1:1 to 500:1; and

the Group VIII metal is platinum, cobalt, ruthenium or palladium.

11. A catalyst solution according to Claim 10 wherein the ratio of gram moles dihydrocarbyl fluorophosphite ligand to gram atoms rhodium is about

5:1 to 150:1; the gram atom ratio of the Group VIII metal:rhodium is in the range of about 1:1 to 5:1; and the hydroformylation solvent is selected from alkanes, cycloalkanes, alkenes, cycloalkenes, carbocyclic aromatic compounds, esters, ketones, acetals and ethers which are liquid at the pressure at which the process is being operated.

12. A process for preparing an aldehyde which comprises contacting an olefin, hydrogen and carbon monoxide with a solution of a catalyst system comprising (1) one or more dihydrocarbyl fluorophosphite compounds having the formula

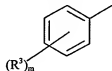


wherein R^1 and R^2 are aromatic hydrocarbyl radicals which contain a total of up to about 40 carbon atoms; (2) rhodium wherein the ratio of gram moles fluorophosphite ligand to gram atoms rhodium is at least 1:1; (3) a Group VIII metal, other than rhodium, or Group VIII metal-containing compound, in an amount effective to reduce the formation of HF during the process; and (4) a hydroformylation solvent.

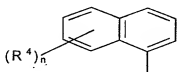
13. Process according to Claim 12 wherein the concentration of rhodium in the solution is in the range of about 30 to 300 mg per liter; the process is carried out at a temperature of about 50 to 135°C and a pressure in the range of 0.7 to 69 bars gauge; and the Group VIII metal is platinum, cobalt, ruthenium or palladium.

14. Process according to Claim 12 wherein the concentration of rhodium in the solution is in the range of about 50 to 300 mg per liter; the process is

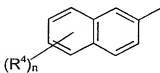
carried out at a temperature of about 50 to 135°C and at a pressure in the range of 0.7 to 69 bars gauge; R^1 and R^2 individually are independently selected aryl groups having the formula:



(II)



(III)



(IV)

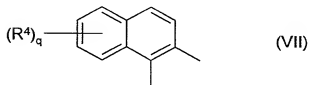
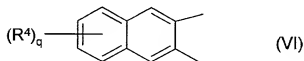
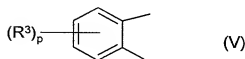
wherein R^3 and R^4 are independently selected from alkyl, alkoxy, halogen, cycloalkoxy, formyl, alkanoyl, cycloalkyl, aryl, aryloxy, aroyl, carboxyl, carboxylate salts, alkoxycarbonyl, alkanoyloxy, cyano, sulfonic acid and sulfonate salts in which the alkyl moiety of such alkyl, alkoxy, alkanoyl, alkoxycarbonyl and alkanoyloxy groups contains up to about 8 carbon atoms; m and n each is 0, 1 or 2; the ratio of gram moles dihydrocarbyl fluorophosphite ligand to gram atoms rhodium is about 1:1 to 500:1; and the Group VIII metal is selected from platinum, cobalt, ruthenium or palladium wherein the gram atom ratio of the Group VIII metal:rhodium metal is in the range of about 1:1 to 5:1.

15. Process according to Claim 12 wherein the olefin is a mono- α -olefin of 2 to 10 carbon atoms.

16. Process according to Claim 14 wherein the olefin is a mono- α -olefin of 2 to 10 carbon atoms.

17. Process according to Claim 12 wherein the concentration of rhodium in the solution is in the range of about 30 to 300 mg per liter; the process is carried out at a temperature of about 50 to 135°C and at a pressure in the range of 0.7 to 69 bars gauge; R^1 and R^2 collectively represent a divalent aromatic hydrocarbylene group containing about 12 to 36 carbon atoms; and the Group VIII metal is selected from platinum, cobalt, ruthenium or palladium.

18. Process according to Claim 17 wherein the ratio of gram moles dihydrocarbyl fluorophosphite ligand to gram atoms rhodium is about 1:1 to 500:1 and R^1 and R^2 collectively represent an arylene group having the formula



or a radical having the formula



wherein

each of A¹ and A² is an arylene radical having formula (V), (VI) or (VII) above wherein each ester oxygen atom of fluorophosphite (I) is bonded to a ring carbon atom of A¹ and A²;

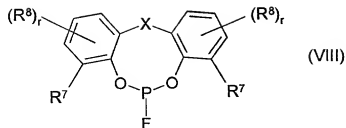
X is (i) a chemical bond directly between ring carbon atoms of A¹ and A²; or (ii) an oxygen atom, a group having the formula -(CH₂)_y wherein y is 2 to 4, or a group having the formula



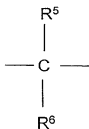
wherein R⁵ is hydrogen, alkyl or aryl; R⁶ is hydrogen or alkyl; and the group -C(R⁵)(R⁶)- contains up to about 8 carbon atoms; and

wherein R³ and R⁴ are independently selected from alkyl, alkoxy, halogen, cycloalkoxy, formyl, alkanoyl, cycloalkyl, aryl, aryloxy, aroyl, carboxyl, carboxylate salts, alkoxycarbonyl, alkanoyloxy, cyano, sulfonic acid and sulfonate salts in which the alkyl moiety of such alkyl, alkoxy, alkanoyl, alkoxycarbonyl and alkanoyloxy groups contains up to about 8 carbon atoms; p and q each is 0, 1 or 2.

19. Process according to Claim 18 wherein dihydrocarbyl fluorophosphite compound has the formula

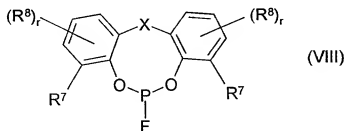


wherein R^7 represents hydrogen, halogen or C_1 to C_{12} alkyl; R^8 represents halogen, C_1 to C_{12} alkyl or C_1 to C_{12} alkoxy; r is 0, 1 or 2; and X is a group having the formula

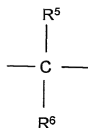


wherein R^5 is hydrogen, alkyl or aryl; and R^6 is hydrogen or alkyl.

20. A process for preparing an aldehyde which comprises contacting an olefin, hydrogen and carbon monoxide with a solution of a catalyst system comprising (1) a dihydrocarbyl fluorophosphite compound of the formula

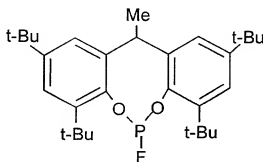


wherein R^7 represents hydrogen, chloro or C_1 to C_4 alkyl; R^8 represents chloro, C_1 to C_4 alkyl or C_1 to C_4 alkoxy; r is 0, 1 or 2; and X is a group having the formula



wherein R⁵ is hydrogen, alkyl or aryl; and R⁶ is hydrogen or alkyl;
 (2) rhodium wherein the ratio of gram moles dihydrocarbyl fluorophosphite ligand to gram atoms rhodium is about 1:1 to 500:1; and (3) a Group VIII metal selected from platinum, cobalt, ruthenium or palladium wherein the gram atom ratio of the Group VIII metal:rhodium metal is in the range of about 1:1 to 5:1; wherein the olefin is a mono- α -olefin of 3 to 8 carbon atoms; and the process is carried out at a temperature of 50 to 135° and the normal to iso ratio of the aldehyde product is controlled by varying the partial pressure of carbon monoxide in the reactor gas between 0.4 and 13 barg.

21. Process according to Claim 20 wherein the concentration of rhodium in the solution is in the range of about 30 to 300 mg per liter; the fluorophosphite ligand has the formula



wherein t-Bu is tertiary butyl and Me is methyl; the ratio of gram moles fluorophosphite ligand to gram atoms rhodium is about 5:1 to 150:1; the olefin is a mono- α -olefin of 2 to 10 carbon atoms; and the process is carried

out at a temperature of about 50 to 135°C at a pressure in the range of 0.7 to 69 bars gauge.

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